Use of Fluorinated Carbonates as Co-Solvents For Lithium-Ion Electrolytes

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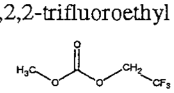
INTRODUCTION

Recently there has been increasing interest in developing lithium-ion electrolytes which possess enhanced safety characteristics, while still able to provide the desired stability and performance. Halogenated solvents have received some attention with the expectation that they will result in the desired improvements. In support of the concept of utilizing halogenated carbonate derivatives, Shu and coworkers[1] have reported results of using of chloroethylene carbonate as a solvent for lithium-ion electrolytes.[2] The same group also investigated fluoroethylene carbonate electrolytes with graphite anodes.[3] It has also been demonstrated that lithium can be intercalated within graphite in trifluoropropylene carbonate (3-trifluoro-methyl-2,5-dioxa-cyclopentan-1-one).[4,5,6] Conductivity and cyclic voltammetric measurements have also been performed on fluoro-carbonate containing electrolyte formulations.[7]

In this paper we would like to disclose recent results relating to the development of lithium-ion electrolytes which contain partially fluorinated carbonate solvents. Specifically, we have demonstrated the beneficial effect of electrolytes which contain the following fluorinated carbonate-based solvents: methyl 2,2,2-trifluorethyl carbonate (MTFEC), _1_, ethyl-2,2,2-trifluorethyl carbonate (ETFEC), _2_, propyl 2,2,2-trifluorethyl carbonate (PTFEC), _3_, methyl-2,2,2,2',2',2'-hexafluoro-*i*-propyl carbonate (MHFPC), _4_, ethyl-2,2,2,2',2',2'-hexafluoro-*i*-propyl carbonate (EHFPC), _5_, and *di*-2,2,2-trifluoroethyl carbonate (DTFEC), _6_.



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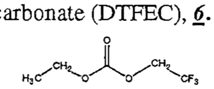

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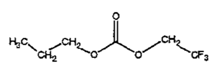

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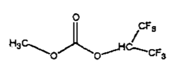

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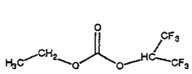

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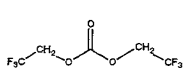

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The advantage of using such solvents is that they possess the requisite stability demonstrated by the hydrocarbon-based carbonates, while also possessing more desirable physical properties imparted by the presence of the fluorine substituents, such as lower melting points, increased stability toward oxidation, and favorable SEI film forming characteristics on carbon. In addition, these solvents can lead to the development of safer lithium ion batteries, due to their low flammability. In order to assess their viability, these co-solvents were blended (20-50 vol/%) with the traditional cyclic and aliphatic carbonates (EC, DEC, DMC, and EMC) and $LiPF_6$ to produce multi-component formulations with the desired properties.

RESULTS AND DISCUSSION

In order to effectively evaluate the potential of such solvents, electrolyte formulations were investigated in both Li-MCMB carbon and MCMB carbon-$LiNiCoO_2$ experimental cells. As shown in Fig. 1, excellent capacities were observed in Li-MCMB cells with a number of electrolyte formulations being comparable to non-halogenated solutions.

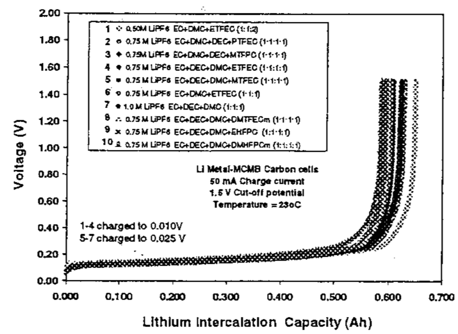

Fig. 1. Fifth lithium de-intercalation of lithium-MCMB cells with different carbonate-based electrolytes.

In addition to studying the charge/discharge characteristics of these cells, a.c. impedance was used to probe the nature of the anode passivating film. It was observed that electrodes in contact with the novel electrolytes displayed low film polarization characteristics as determined from the low R_{ct} values observed. In addition to EIS measurements, DC micropolarization techniques were also employed to study the charge transfer behavior of the passivating films on the MCMB electrodes at various temperatures. The polarization resistance, which was calculated from the slopes of the linear plots generated under potentiodynamic conditions, was consistently lower for the cells possessing fluorinated carbonate- containing electrolytes compared to the alkyl-carbonate-based systems, being especially dramatic at low temperatures. This implies that the use of fluorinated carbonate-containing electrolytes leads to improved SEI characteristics, with enhanced lithium kinetics. These aspects, in part, explain the excellent low temperature performance observed in some cases.

ACKNOWLEDGEMENT

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